CEMENT LIME MANUFACTURE

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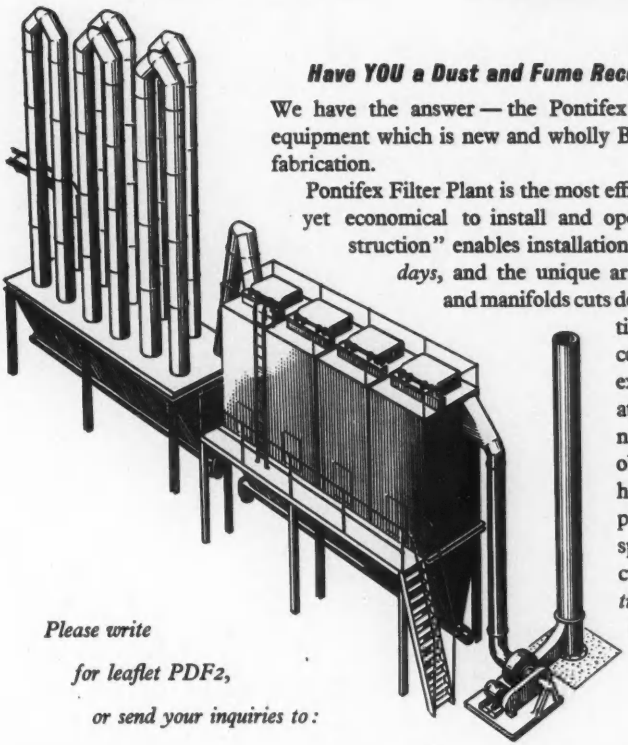

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VOLUME XXXI. NUMBER 1. JANUARY, 1958

Uttar Pradesh Cement Works, India.

By H. SWIFT, M.I.Mech.E., M.Inst.B.E.
OF HENRY POOLEY, CONSULTING ENGINEERS, AND GENERAL MANAGER OF THE WORKS.

Introduction.

THE recent growth of the cement industry in India has been very rapid. In the year 1947 1½ million tons of cement were produced. At the beginning of the first five-year plan (1951-56) production was 3,000,000 tons, and at the end of that period it was 6,000,000 tons. Further expansion is provided for in the second five-year plan (1956-61) and it is expected that at the end of this period production will be about 12,000,000 tons.

The production of cement in India is not well distributed and vast areas of the country obtain supplies from long distances, involving high transport costs. Uttar Pradesh, the third largest State in India, with an area of 113,409 square miles and a population of more than 63,000,000, had no cement factory. In view of the large development programme in the State, including the Rihand dam which alone will require 450,000 tons of cement, the Government of Uttar Pradesh decided to build India's first State-Government-controlled cement factory.

The factory (*Figs.* 1 and 2) is in the southern part of the State, in the village of Churk in the Mirzapur district, and is connected by a railway fifty miles long to Chunar on the main Delhi-Calcutta Railway with branch connections to the Northern Railway. The factory is therefore well situated to supply the densely-populated southern areas of the State as well as Lucknow and the Northern Province. The factory has a rated capacity of 700 tons of cement a day by the wet process. It has its own power station, and is designed so that the capacity can be doubled without interfering with production and at relatively little cost.

In the year 1949 an order was placed with Messrs. Vickers-Armstrongs, Ltd., for complete cement-making machinery, including power station, electrical equipment, ropeway and steel-frame buildings. The civil engineering work was done by a local contractor, under the supervision of the Public Works Department of the

State Government. The factory was completed in August 1954 under the management of Messrs. Henry Pooley, consulting engineers, who managed the factory for three years and who are providing the managerial and technical staff. They also acted as consulting engineers to the State Government during the last two years of the building of the factory.

Raw Materials.

The raw materials used are limestone, shale, and laterite.

Limestone and shale are present in the same deposit in State-owned quarries near Markundi, about 2¾ miles from the factory. The limestone is of the Rohtas stage of the Semri series, which is of Vindhyan formation. The thickness of the

Fig. 1.—General View.

deposit varies from 30 ft. to 300 ft.; it is dark grey in colour, medium grained in structure, and interbedded with bands of shale; the layers of limestone vary in thickness from 1 in. to 10 ft. and the layers of shale are up to 2 ft. thick. The deposits now being worked will satisfy the needs of the factory for forty-six years at the present rate of output.

About 2 per cent. of laterite is added to the raw material and is available in abundant quantities at State-owned deposits about thirty miles from the works.

A typical analysis of the limestone, shale, and laterite is given in *Table I*.

TABLE I

	High-grade limestone	Low-grade limestone	Shale	Laterite
Loss	39·70	35·90	20·80	2·75
Silica	7·30	14·10	39·80	29·10
Alumina	1·90	3·90	9·92	25·27
Iron	0·90	1·10	3·00	39·48
Lime	49·00	43·00	23·00	1·00
Magnesia	1·00	1·30	1·83	—
Alkalis and loss	0·20	0·70	—	—

Coal is obtained from Karanpura (Bihar) about 400 miles from the factory. It is a high-volatile screened slack with an analysis on an air-dry basis as follows: Moisture, 4 per cent.; ash, 17·46 per cent.; volatile matter, 31·8 per cent.; fixed carbon, 48·74 per cent. The calorific value is 12,100 B.t.u.'s.

Gypsum is obtained from Bikaner (Rajasthan), about 800 miles from the works. It is of the amorphous variety, having an average content of $CaSO_4 2H_2O$ of 82 per cent., and varies in size as received from dust to 2-ft. cubes.

THE QUARRY.—The limestone deposit has a height of about 130 ft. from the floor of the quarry and is capped with a layer of earth, sandstone and decomposed shale with a thickness of about 20 ft. Throughout its height the bands of limestone vary widely in chemical composition, and for this reason, and also because of the layers of shale, much labour is employed in selecting the limestone and the removal of excess shale, which is present in greater proportion than is required. The deposit yields about 60 per cent. of limestone and about 40 per cent. of shale. As the disposition of the layers of shale varies throughout the height, two methods of quarrying are used. On the lower 50 ft. of the face machines are used, as the layers of shale are thinner and less numerous; on the upper 80 ft. the layers of shale are thicker and more numerous, and quarrying is by hand.

The quarry is worked on the bench system. The upper three benches are worked manually, the overburden, stone, and shale being drilled by jack-hammers, blasted, sorted, and loaded into decauville tubs of 1 cu. yd. capacity on 24-in. track. The tubs are moved by diesel-driven locomotives of 25 h.p. The limestone is discharged over the edge of the lower bench to form a stock-pile, from which it is taken to the crushing plant, and the surplus shale, sandstone, and overburden are removed to waste dumps.

Wagon-drills with 4-in. drifters are used for drilling the lower 50 ft. bench, compressed air being supplied by six portable diesel-driven compressors each of 205 cu. ft. capacity. The selected hand-quarried material from the upper benches and the composite material from the lower bench are removed by two 1½ cu. yd. electrically-driven shovels and loaded into Euclid rear-end dumpers of 15 tons capacity. The five shovels and dumpers in use are capable of loading and hauling material to the crusher at the rate of 200 tons per hour from the farthest point of the quarry, which is about one mile from the crushing plant.

CRUSHING THE STONE.—Limestone in pieces up to 30 in. cube is discharged into a receiving hopper built of steel and situated at ground level, with a capacity of about 22½ tons (one and a half dumper loads). Discharge from the hopper is controlled by heavy curtain chains in front of a swinging-gate.

From the feed-hopper the stone is conveyed to the primary crusher by an apron-feeder 54 in. wide. The trays are of $\frac{5}{16}$ in. mild steel plate. Fixed to the underside are two sets of steel chains and five sets of cast-iron rollers; the outer rollers are flanged to guide the trays along the track. The feeder is driven through a counter-shaft and a worm reduction-gear by a 15-h.p., 360 to 720 r.p.m., variable-speed motor. The primary crusher has a jaw opening of 60 in. by 48 in. and is capable

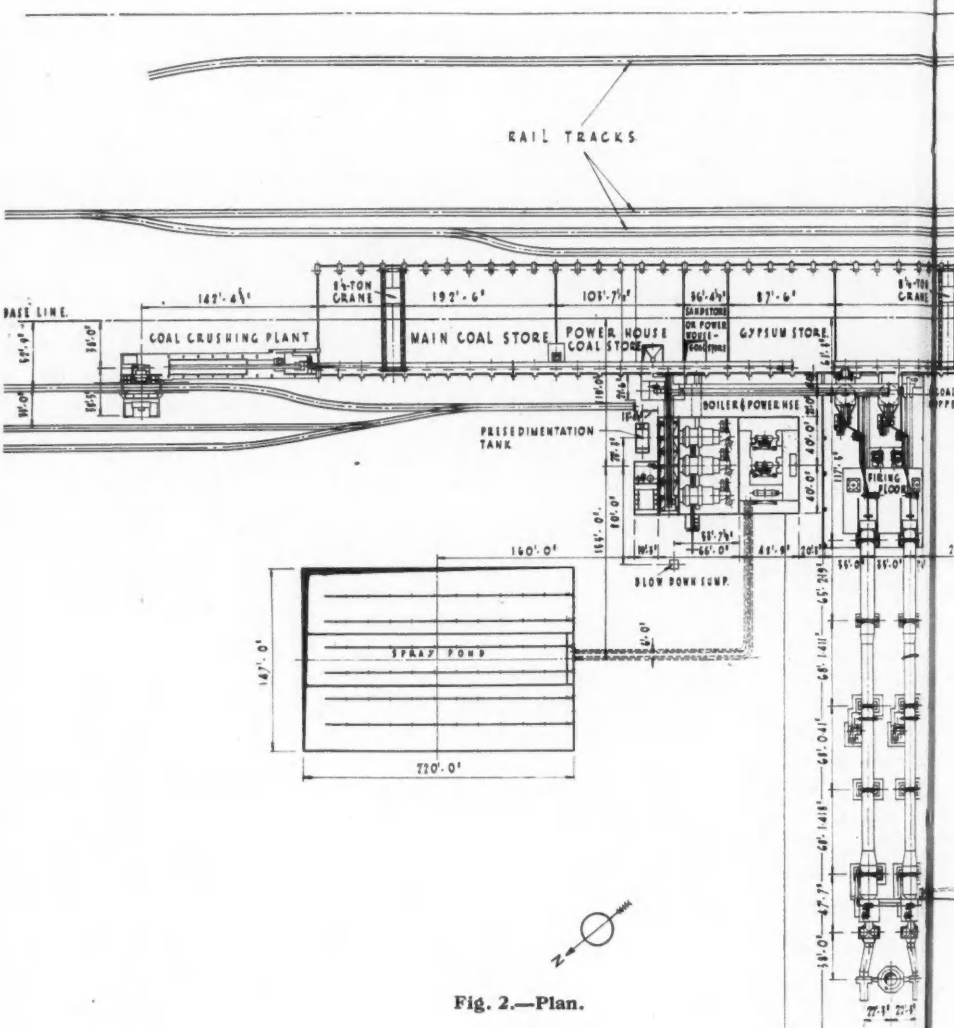
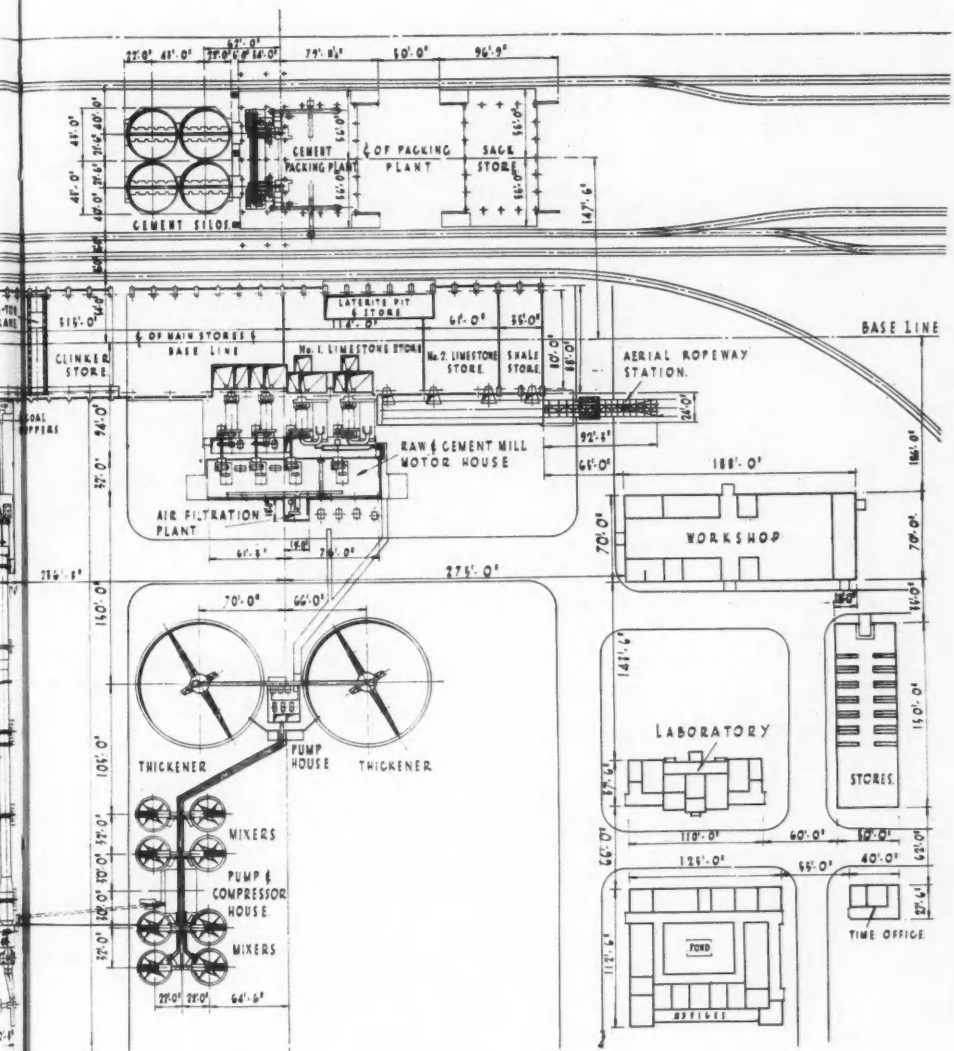

RAIL TRACKS
BASE LINE
142'-4½"
8½-TON CRANE
192'-6"
105'-7½"
86'-4½"
87'-6"
COAL CRUSHING PLANT
MAIN COAL STORE
POWER HOUSE COAL STORE
GYPSUM STORE
BOILER & POWER HSE
PRESEDIMENTATION TANK
FIRING FLOOR
160'-0"
BLOW DOWN SUMP
SPRAY POND
147'-0"
720'-0"

Fig. 2.—Plan.


CEMENT SILOS
CEMENT PACKING PLANT
℄ OF PACKING PLANT
SACK STORE
CLINKER STORE
℄ OF MAIN STORES & BASE LINE
LATERITE PIT & STORE
No. 1. LIMESTONE STORE
No. 2. LIMESTONE STORE
SHALE STORE
BASE LINE
AERIAL ROPEWAY STATION.
RAW & CEMENT MILL MOTOR HOUSE
AIR FILTRATION PLANT
WORKSHOP
LABORATORY
STORES
TIME OFFICE
THICKENER
PUMP HOUSE
THICKENER
MIXERS
PUMP & COMPRESSOR HOUSE
MIXERS
POND
OFFICES

of reducing 30-in. cubes to 8 in. and smaller at the rate of 200 tons an hour. The sectional frame of the crusher is of cast steel and is held together by rolled-steel tie-bolts. The front toggle-plate is sectional and fitted with shearing bolts to prevent damage by tramp-iron entering the crusher with the stone. The Pitman bearings and the frame bearings are lined with white metal, are water cooled, and have automatic lubrication. The crusher is driven by vee-ropes operated by a 220-h.p., 580 r.p.m., motor.

The crushed stone is discharged through a steel chute on to an inclined troughed-belt conveyor 40 in. wide by 120 ft. long, driven through worm reduction-gearing by a 15-h.p., 720 r.p.m., motor; ratchet gear is fitted to the head-shaft of the conveyor to prevent it from running back on stopping. The stone from the conveyor passes over a 48-in. by 102-in. double-deck Gyrex vibrating screen. The upper screen is of 3-in. square mesh and the lower screen of 1-in. mesh. At first the material passing the 1-in. screen was by-passed directly to the crushed-stone belt and so relieved the load on the secondary crusher; it was found, however, that the mechanically-quarried stone contained small pieces of shale and top soil in sufficient quantity to reduce the total carbonate content by 5 per cent.; in order to prevent this material passing to the works, the 1-in. screen was replaced by a screen with $\frac{1}{2}$-in. mesh, and the material passing this screen was directed through a chute to a short belt-conveyor from whence it was removed to tip. The 8-in. to $\frac{1}{2}$-in. stone is passed to a size SXT 14-48 Pennsylvania hammer-mill, which reduces it so that about 85 per cent. is smaller than $\frac{3}{4}$ in.

The hammer-mill is directly coupled through a Bibby coupling to a 360-h.p., 960 r.p.m., motor. The crushed stone is discharged through a steel chute on to an inclined and horizontal belt-conveyor, 30 in. wide and 327 ft. long; the inclined part lifts the stone to a height of 38 ft., where it is discharged by a travelling throw-off carriage into storage bunkers. The conveyor is driven through a tandem drive from a worm reduction-gear by a 30-h.p., 720 r.p.m., motor. The storage bunkers are of reinforced concrete and have a capacity of 8,000 tons and a total length of 150 ft.; partitions form six compartments, each of which is provided with two discharge-valves for delivering to the ropeway. The primary and secondary crusher and vibrating screen are in reinforced concrete structures and the conveyors are in covered gantries.

ROPEWAY.—The stone of $\frac{3}{4}$ in. size and smaller is transferred from the stock-pile at the crushing plant to the factory by a two-cable aerial ropeway (*Fig.* 3) having a total length of about $2\frac{3}{4}$ miles and capable of transporting 200 tons per hour in tipping buckets of $27\frac{1}{2}$ cwt. capacity. The buckets travel at 160 yd. per minute and are placed on to the rope at 66-yd. intervals by an automatic spacer. The ropeway is driven by two motors in tandem; a 80-h.p., 730 r.p.m., motor is connected through a 4 to 1 reduction gear-box by a ratchet-type coupling to the main drive-shaft, which is driven by a 230-h.p., 730 r.p.m., motor. The motors are controlled by sequence-timing contactor-gear which provides an almost uniform acceleration of the rope. The smaller motor is started first and, when at full

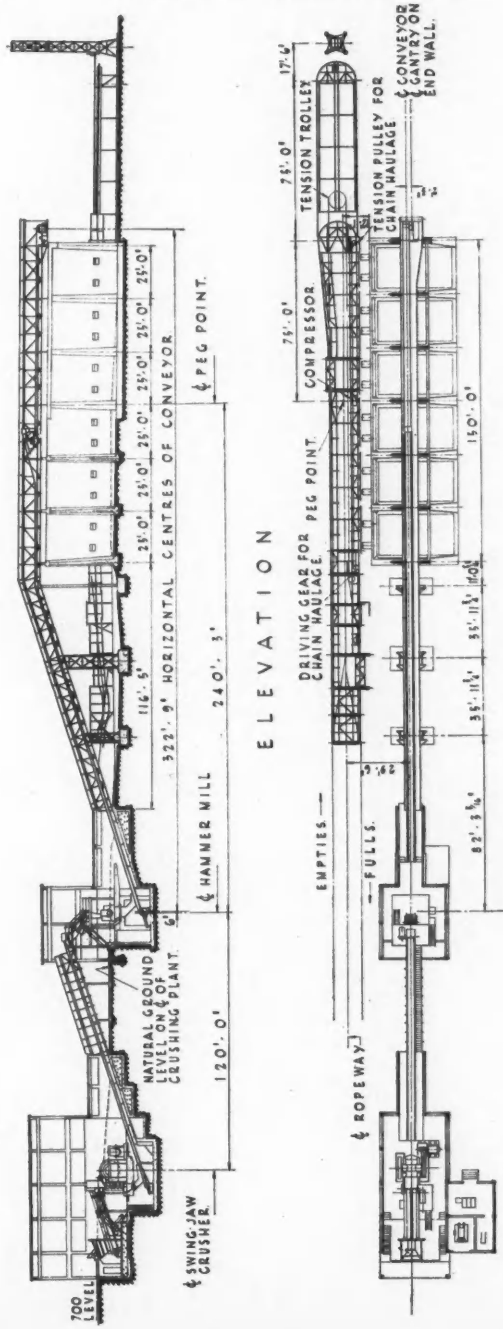


Fig. 3.—Arrangement for Transporting Raw Material.

speed, moves the rope through the 4 to 1 reduction-gear to one-fourth of the normal speed; after a predetermined time the larger motor is automatically started at an initial speed coinciding with that of the moving rope and gradually increases in speed at timed intervals until the maximum speed is reached. Immediately the load is transferred to the main motor the smaller motor is automatically stopped and disconnected from the main drive-shaft through the ratchet-type coupling. A magnetic brake and a ratchet-type device are fixed on the drive-shaft of the main motor to arrest the rope on stopping and prevent the running back of the loaded buckets, which are 122 yd. higher at the driving end.

At the quarry the empty buckets are moved slowly in front of the discharge chutes of the storage bunkers, and at any selected point the buckets are automatically released for filling. When they are full the buckets move on to an automatic spacer and are placed on the rope at timed intervals. At the factory the full buckets are automatically unlocked from the rope and slowly passed to the mill feed-bunkers or directly into storage.

Main Stores Building.

The main stores building (*Fig.* 4), in which limestone, shale, gypsum, cement clinker, boiler ashes, and coal are stored, is a steel-framed structure 945 ft. long, 80 ft. wide between crane rails, 48 ft. high to crane rails, and 63 ft. high to eaves. The main columns are on reinforced concrete piers 15 ft. high with reinforced concrete panels 12 ft. high between the columns to form a retaining wall around the building. Reinforced concrete partitions form compartments for the different materials. Two tunnels 10 ft. wide traverse the store; these give access to both sides of the building, and also accommodate the cement transport lines from the cement mills to the cement silos, water mains, and cables. Two overhead electric cranes of 80 ft. span and 8½ tons capacity, each fitted with a grab of the four-rope type with

Fig. 4.—Main Store.

a capacity of 110/88 cu. ft., traverse the store for distributing the materials inside the building and also for delivering limestone and shale to the raw mills, cement clinker and gypsum to the cement mills, coal to the boiler house and kilns, and ashes to railway wagons for disposal. The cranes have three motors; the motor for raising and lowering the grab at a speed of 150 ft. per minute is a 130-h.p., 735 r.p.m., machine; the motor for moving the crane along the track at 400 ft. per minute is a 50-h.p., 730 r.p.m. machine; a 15-h.p., 725 r.p.m. motor moves the grab across the building at speed of 200 ft. per minute. Limit-switches are fitted for both transverse and longitudinal travel, and the controls for the motors are in the driver's cab which travels with the crane; anti-collision gear is fitted to both cranes. On one side of the building is a lean-to over the raw mills and the cement mills. Inside the store and adjacent to the mills are reinforced concrete bunkers for raw materials and cement clinker. Another reinforced concrete bunker inside the store contains coal for the kilns and boilers, while another is used for discharging boiler ashes to railway wagons for disposal.

Handling Coal and Gypsum.

Coal and gypsum are received in railway wagons of 22 tons capacity and passed on to a wagon-tippler (by Strachan & Henshaw) with a capacity of ten wagons per hour. From the tippler the material falls into a reinforced concrete hopper of about 40 tons capacity situated at ground level, from which a swinging gate fitted to the outlet of the hopper regulates the delivery of the material to an inclined apron-conveyor 48 in. wide. The trays of the conveyor are of $\frac{3}{16}$-in. mild steel plate linked by two strands of steel chain mounted on four sets of rollers on steel tracks. The drive to the conveyor is through a counter-shaft to a worm reduction-gear to which is attached a 10-h.p., variable-speed, 720-360 r.p.m. motor. The coal or gypsum falls from this conveyor through a steel chute on to an inclined troughed-belt conveyor 36 in. wide, driven through worm reduction-gear connected to the head-shaft by a 12-h.p., 720 r.p.m. motor, and is discharged into a 24-in. by 40-in. single-roll crusher which is capable of reducing coal or gypsum from 12 in. to minus 2 in. at the rate of 60 tons per hour. The roll and the adjustable breaker-plate are of manganese steel, and a safety device is fitted to the flywheel to prevent damage by tramp-iron passing into the crusher. The crusher is driven through vee-ropes by a 65-h.p., 725 r.p.m. motor. The crushed coal or gypsum passes from the crusher through a steel chute to a totally-enclosed vertical bucket elevator 24 in. wide by which is it elevated and discharged on to an inclined and horizontal belt-conveyor 24 in. wide and 374 ft. long; this conveyor is carried by the columns of the building at a height of 37 ft. and distributes coal and gypsum through a travelling throw-off carriage directly into store, or takes the coal either to a screening plant or to the bunker for delivery to the boiler-house and kilns. The elevator is driven by a 15-h.p., 720 r.p.m. motor and the conveyor by a 15-h.p., 725 r.p.m. motor.

To obtain screened coal of the size required for the boilers, coal is discharged from the throw-off carriage into the chute of a 48-in. by 78-in. double-deck Gyrex

vibrating screen, where all coal larger than 1 in. and smaller than $\frac{1}{8}$ in. is screened out and discharged into storage for the kiln; the coal between 1 in. and $\frac{1}{8}$ in. is discharged into storage for the boiler. The screen is driven through vee-ropes by a 5-h.p., 960 r.p.m. motor.

Coal for either the boilers or the kilns is grabbed by the overhead cranes from the stock-piles and discharged into a reinforced concrete hopper of about 50 tons capacity, from which it is extracted through a swinging-gate by an inclined apron-feeder 48 in. wide, and of similar construction to the feeder at the wagon-tippler hopper discharge. The conveyor is driven through a worm reduction-gear by a 10-h.p., 720 r.p.m. motor. The coal passes from the apron-feeder through a steel chute to a vertical enclosed elevator with buckets 24 in. wide. From the elevator the coal is discharged on to either of the two belt conveyors; one conveyor, inclined and horizontal, with a flat belt 30 in. wide by 180 ft. long, is for discharging into either of the two coal bunkers for the kiln; the other conveyor is horizontal, has a flat belt 24 in. wide by 109 ft. 3 in. long, is provided with steel ploughs for discharging into either of the three feed-bunkers for the boiler, and is arranged so that it can also receive coal direct from the wagon-tippler or from the throw-off carriage. A steel plough is also arranged on this conveyor for transferring the coal on to the conveyor supplying the kiln coal-bunkers. The elevator is driven through a worm reduction-gear by a 15-h.p. motor running at 720 r.p.m. The conveyor supplying the kiln coal-bunkers is driven by a worm reduction-gear connected to the head-shaft by a 12-h.p., 720 r.p.m. motor, and the conveyor supplying the boilers is driven in a similar manner by a $7\frac{1}{2}$-h.p., 720 r.p.m. motor.

(To be continued.)

Cement Production in Sicily.

A cement works near Palermo, with an annual capacity of 1,500,000 quintals, was started in October 1957. Production of cement in Sicily increased from 200,000 tons in 1952 to 700,000 tons in 1956, and is expected to be 1,000,000 tons in 1958.

Proposed New Works in Ceylon.

It is reported that the Government of Ceylon is considering the erection of a cement works, with an annual capacity of 60,000 tons, at Puttalam. The Kankesan Cement Works Corporation proposes to install a new kiln at its works at Kankesan.

New Cement Works in Korea.

A cement works at Mungyong, Korea, recently started production. The factory was built with United States aid, at a cost of 95,000,000 Danish kroner, by Messrs. F. L. Smidth & Co.

Determination of Calcium Oxide.

IN a tentative revision of the Standard Methods of Chemical Analysis of Portland Cement of the American Society for Testing Materials, the following method is given of ascertaining the content of free calcium oxide in fresh Portland cement clinker. When the method is applied to Portland cement or aged clinker, the possibility of the presence of calcium hydroxide should be kept in mind as the method does not differentiate between free calcium oxide (CaO) and free calcium hydroxide ($Ca(OH)_2$). The method is based on the solution of free calcium oxide in a hot solution of glycerol and alcohol and the subsequent titration of the dissolved lime with an alcoholic solution of ammonium acetate.

APPARATUS.—It is recommended that all parts of the boiling assembly have standard-taper interchangeable ground-glass joints, although connections with clean tight-fitting rubber stoppers are permissible. The flask used for boiling the sample and solution is a flat-bottom short-neck boiling flask or Erlenmeyer flask of 200 or 250 ml. capacity. The reflux condenser has a length of at least 300 mm. if water-cooled or 500 mm. if air-cooled.

A burette of 10-ml. capacity and graduated in units of not more than 0·05 ml. is required. A refilling type of semi-micro burette with a 100-ml. reservoir is recommended, and the air entering the reservoir should pass through a protective tube containing soda-asbestos (Ascarite) and anhydrous calcium sulphate (Drierite), or other suitable agents, for removal of carbon dioxide and moisture.

REAGENTS.—It is essential that the reagents and subsequent solutions be protected from moisture and carbon dioxide. Ammonium acetate is usually damp upon receipt or after laboratory storage and must be dried before use. Desiccation drying is recommended for a period of not less than two weeks, using anhydrous calcium sulphate or other drying agents of equal efficiency. If the ammonium acetate appears damp after this storage period, the presence of free acetic acid is denoted and a fresh supply of ammonium acetate must be used.

Prepare a standard solution of ammonium acetate ($NH_4C_2H_3O_2$) by dissolving 16 g. of desiccated ammonium acetate in 1 litre of ethanol in a dry, clean, stoppered bottle. Standardize this solution as follows:

Ignite approximately 0·1 gr. of calcium carbonate ($CaCO_3$) or calcium oxalate (CaC_2O_4) in a platinum crucible at 900 to 1,000 deg. C., cool the contents in a desiccator, and weigh to the nearest 0·0001 gr. to constant weight. The weighings must be performed quickly to prevent absorption of water and carbon dioxide (CO_2). Immediately transfer the CaO without grinding to a clean and dry 200-ml. or 250-ml. Erlenmeyer flask and reweigh the empty crucible to determine the weight of CaO used to the nearest 0·0001 gr. Add to the flask 60 ml. of glycerol-ethanol solvent and a few glass beads to ensure vigorous boiling and complete agitation without bumping when heat is applied. Disperse the CaO in the solution by shaking the flask, and attach a reflux condenser. Boil and titrate as directed

later. The titration is complete when the pink colour does not appear in the solution during continuous boiling for 1 hour. (Titrations should be conducted at 5-minute intervals for the first 20 minutes to prevent the formation of crystals (probably calcium glyceride) which dissolve slowly and increase the time required for the completion of the titration. Thereafter, the colour of the solution should be used as a guide for the titration interval.) If the end-point is accurately determined the solution will turn pink upon cooling, since the end point will not be the same for a hot and a cold solution. This is evidence that the end-point has not been greatly exceeded.

Calculate the CaO equivalent of the ammonium acetate solution in grammes per millilitre by dividing the weight of CaO used by the volume of solution required.

Absolute ethanol is preferred but may be replaced by anhydrous ethanol denatured according to Formula No. 3a or 2b of the U.S. Bureau of Internal Revenue. The Formula 3a alcohol is 95 per cent. ethanol and 5 per cent. methanol, and the Formula No. 2b alcohol is 99·5 per cent. ethanol and 0·5 per cent. benzol.

Water is usually present in glycerol. To ensure that the water content is under 5 per cent. the specific gravity at 25/25 deg. C. should be determined by means of a pycnometer and should not be less than 1·249.

Prepare a solution of 1 volume of glycerol and 5 volumes of ethanol. To a clean and thoroughly dried 2½-litre reagent bottle, add 1 lb. of glycerol (360 ml.) and 1,800 ml. of ethanol, using the ethanol as a rinse for the glycerol to ensure its complete transfer. To this mixture add 0·18 gr. of phenol-phthalein. Immediately stopper the bottle and warm slightly on a surface that is less than 250 deg. F. Localized heating is prevented by frequent agitation, until the indicator is completely dissolved and thoroughly mixed.

The solvent mixture is slightly alkaline, as indicated by a faint pink colour when cooled to room temperature. If the mixture is colourless, add gradually a freshly prepared solution of sodium hydroxide (NaOH) in ethanol until a faint pink is formed. An approved neutral point is reached when the faint pink colour of 60 ml. of the solvent mixture disappears on boiling or can be dispelled by not more than 0·02 ml. (about 1 drop) of ammonium acetate solution (1 ml. = 0·005 gr. CaO). (The error resulting from an excess alkalinity equivalent to 0·02 ml. of ammonium acetate solution is only 0·01 per cent. of free CaO and may be disregarded.) If the colour of the fresh solvent mixture is strong pink when cooled to room temperature, dispel the colour by the addition of small increments of ammonium acetate solution until the faint pink colour specified is attained. If the solvent mixture becomes acid on standing, as indicated by the disappearance of the faint pink colour, the alkalinity must be readjusted to a faint pink by the gradual addition of a freshly prepared solution of NaOH in ethanol.

PROCEDURE.—Grind about 1·2 gr. of the sample in an agate mortar for 5 minutes. (Thorough grinding of the sample is essential for proper exposure of the free lime grains that often are occluded in crystals of tricalcium silicate in the

cement. However, exposure of the sample to the air must be kept at a minimum to prevent carbonation of the free lime. In particular, direct breathing into the sample must be avoided. The sample should be sufficiently fine to pass easily a No. 200 (74-micron) sieve, but sieving is not recommended. If the sample is not to be immediately tested, it must be kept in an airtight container to avoid unnecessary exposure to the atmosphere.) Weigh 1 gr. of the finely ground sample into a clean and dry 200-ml. or 250-ml. Erlenmeyer flask, add 60 ml. of the glycerol-ethanol solvent and a few glass beads, and agitate to disperse the sample. Attach a reflux condenser and boil the solution in the flask on a hot plate or other suitable source of heat. (The use of an open gas flame for boiling the solvent-sample mixture presents a fire hazard and therefore is not recommended.) Vigorous boiling is more essential with cement than with the pure CaO used in standardizing the acetate solution, and should be conducted so as not to necessitate shaking of the flask.

Remove the condenser and immediately titrate the solution, while near boiling, with ammonium acetate solution (1 ml. = 0·005 gr. CaO). (If it is necessary to leave the determination uncompleted, remove the flask from the condenser, titrate to a faint pink colour, and stopper the flask tightly. When resuming the determination, boil the mixture before continuing the titration.) A slight pink colour should remain after all but the final titration, since excess acetate solution reacts with the calcium aluminate and silicates present in the sample.

Return the flask to the hot plate, attach the condenser, and boil as before. Repeat the titration and boiling cycles at periodic intervals, whenever the solution turns deeply pink or red, depending upon the speed of the solution of the free CaO. Titrations may be as frequent as five minutes but should never exceed 20 minutes in the early stages. Continue titration until the faint pink colour from the previous titration does not deepen and the percentage of free CaO of the sample does not increase by more than 0·05 upon its discharge with the acetate solution after 2 hours of boiling. A strong daylight lamp with a reflector may be used as an aid in the discernment of the end-point by matching the contents of the flask with similar contents in another flask that contains an excess of ammonium acetate.

CALCULATIONS.—Calculate the percentage of free CaO to the nearest 0·1 as follows: Free CaO (per cent.)$=EV\times 100$, in which E is the CaO equivalent of the ammonium acetate solution in grammes per millilitre, and $V=$ millilitres of ammonium acetate solution required by the sample.

Duplicate determinations by this method should agree within 0·2. The maximum permissible variation between the extreme values in triplicate determinations should be less than 0·3.

Optional Method

An optional method is given which is identical with the method described in the foregoing except that it utilizes an accelerator in the extraction solvent to hasten solution of the free calcium oxide.

REAGENTS.—Anhydrous barium chloride ($BaCl_2$), anhydrous strontium nitrate ($Sr(NO_3)_2$), or sodium chloride (NaCl) may be used as the accelerator. When $BaCl_2$ or $Sr(NO_3)_2$ are used they are added to the glycerol-ethanol solvent before the neutralization is performed in amounts of 36 g. and 22 g. per batch respectively. A convenient way to prepare a large amount of solvent is to heat $BaCl_2 \cdot 2H_2O$ at 120 to 130 deg. C. for several hours, dissolve it in hot glycerol (100 to 125 deg. C.) without grinding, and mix the solution with ethanol. (If the salt is dehydrated at a much higher temperature it may be slow to dissolve in hot glycerol or solvent, even when ground.) When sodium chloride (NaCl) is used, 0·5 gr. is added directly to the flask containing the sample and the solvent.

Prepare and standardize a solution of ammonium acetate as described previously, except that the solvent prepared for or with the selected accelerator must be used to dissolve the CaO.

Ammonium acetate, ethanol, and glycerol may be used as previously described.

Glycerol-ethanol solvent is as already described, except that the selected accelerator must be added as described for this optional method.

PROCEDURE.—Determine the free CaO in clinker or cement as already directed, with the following exceptions: (1) Use the selected accelerator as directed for this optional method. (2) The end-point is considered to be reached when the faint pink colour from the previous titration does not deepen and the free CaO content of the sample does not increase by more than 0·05 per cent. upon its discharge with the acetate solution during the last hour of boiling. If the boiling is too prolonged the sample may be partially decomposed and the end-point may be obscured by coloured decomposition products.

The results obtained by this method generally are slightly higher than those obtained by the method first described. Duplicated determinations should agree within 0·20. The maximum permissible variation between the extreme values in triplicate determinations should be less than 0·3.

Cauldon Cement Works.

We are asked to state that P.H.I. Engineering, Ltd., is an independent British concern, and not the agent of any British or German firm. They are the main licensees for Great Britain and the Commonwealth of Dipl. Ing. Max Berz and Messrs. Gebr. Pfeiffer Barbarossawerke A.G., of Kaiserslautern, who own the basic British and other patents for MB-mills. The two raw meal mills and the coal mill at Cauldon Cement Works (see this journal for November 1957) were manufactured in Germany to the order of P.H.I. Engineering Ltd.

New Cement Works in Italy.

A cement works with a capacity of 500,000 tons a year is being built at Araquata Scrivia, Liguria, Italy.

Monocalcium Aluminate Hydrate in Cement.

In an introduction to a report on research on the presence in cement of monocalcium aluminate hydrate, Mr. Elmer T. Carlson states, in the Journal of Research of the U.S. National Bureau of Standards for August 1957, that the existence of a monocalcium aluminate hydrate has been for many years a matter of uncertainty. More than twenty years ago, Assarsson reported the preparation of a compound having the composition $CaO{\cdot}Al_2O_3{\cdot}10H_2O$. It was obtained in the form of a gel by the action of water on anhydrous calcium aluminates and high-alumina cements. Although Assarsson gave an X-ray diffraction powder pattern for the material, this was not conclusive evidence of the existence of a monocalcium aluminate hydrate. A number of other hydrated calcium aluminates give somewhat similar patterns, and the gel might have been a mixture of two or more phases. More recently, Longuet reported the preparation of a compound for which he indicated the formula $CaO{\cdot}Al_2O_3{\cdot}7H_2O$ as most probable. He also gave an X-ray diffraction pattern differing in several respects from that given by Assarsson. The two patterns probably can be reconciled, and patterns agreeing in general with that of Longuet have been obtained at the Bureau on hydrated pastes of high-alumina cements and of monocalcium aluminate. Because of the probable importance of this compound in the setting and hardening of high-alumina cements, some additional work was undertaken in an attempt to obtain the hydrate in better crystallized form.

While this study was in progress, two additional investigations bearing on the subject were reported. In the revised edition of "The Chemistry of Cement and Concrete" Lea gives an X-ray diffraction pattern obtained by H. G. Midgley for $CaO{\cdot}Al_2O_3{\cdot}10H_2O$. The pattern agrees fairly well with the more abbreviated patterns given by both Assarsson and Longuet. Farran developed a method for the study of crystal formation at the interface between cement and aggregate, and by this means obtained crystals of a monocalcium aluminate hydrate large enough for a determination of its optical properties and shape. The crystals grew from a paste of high-alumina cement, and the hydration product contained small amounts of one or more other phases. Farran also published an X-ray pattern for his preparation. The existence of a monocalcium aluminate hydrate thus seems established. Because of the close relationship between calcium and strontium, it was considered of interest to determine whether a monostrontium aluminate hydrate also can be prepared.

Summarising the results of the tests, the author states that monocalcium aluminate hydrate, probably having the composition $CaO{\cdot}Al_2O_3{\cdot}10H_2O$, was prepared by precipitation from calcium aluminate solutions at approximately 1 deg. C., and by hydration of pastes of monocalcium aluminate and of high-alumina cement at 1 deg. and 25 deg. C. Under conditions favourable for slow crystal growth, this hydrate crystallized as hexagonal prisms with terminal pyramids. They were very weakly birefringent, with a mean refractive index

of 1·471. Drying over calcium chloride reduced the water of hydration to $7H_2O$, and the indices and birefringence increased, but the X-ray pattern was apparently unchanged. An analogous monostrontium aluminate hydrate was prepared by similar methods, but it was obtained only as minute needles or prisms. Like the calcium analogue, it probably crystallizes with 10 molecules of H_2O, 3 of which may be removed by drying over calcium chloride. The mean index of refraction is about 1·478. When placed in a humid atmosphere at room temperature it decomposed, with the formation of $3SrO{\cdot}Al_2O_3{\cdot}6H_2O$ and $Al_2O_3{\cdot}3H_2O$ (gibbsite). X-ray powder diffraction patterns are given for both monocalcium aluminate hydrate and monostrontium aluminate hydrate. The similarity between the two is apparent.

Barium and Strontium Cements

IN "Zement-Kalk-Gips" for May, 1957, A. Braniski describes experiments with cements in which the calcium content of Portland and high-alumina cements is replaced by barium or strontium, or both. Satisfactory cements were made with natural barium and strontium carbonates, but the cements used for tests were made with synthetic carbonates to avoid the presence of lime and magnesia.

A few hundred kilogrammes of the clinker of barium cement, strontium cement, and barium-high-alumina cement were made in a furnace arranged to allow the product to cool rapidly. Smaller amounts of strontium-high-alumina cement and strontium-barium-high-alumina cement were made in a laboratory muffle. The sintered cements were burnt at temperatures of 1,460 deg. C. to 1,530 deg. C., and the fused cements were formed at undetermined higher temperatures. The only one of these cements that could be made at a temperature lower than that required for Portland cement was a barium-high-alumina cement rich in iron oxide. Rapid cooling is said to be essential in all cases. The clinkers were ground finely in a porcelain mill; the clinkers of the fused cements were extremely hard and difficult to grind.

A blastfurnace-slag-barium cement was made by mixing 70 per cent. of slag and 30 per cent. of barium-cement clinker, with and without the addition of gypsum. This had a minimum compressive strength of 327 kg. per square centimetre at seven days when tested by the standard German method. The addition of 5 per cent. of gypsum reduced the shrinkage as a result of the expansive formation of barium sulphate. In the mixture containing 30 per cent. of slag and 70 per cent. of clinker the minimum compressive strength at seven days was 360 kg. per square centimetre. The corresponding strontium cements had somewhat lower strengths.

Concrete prisms made with these cements were submerged in the Black Sea for fifteen years together with prisms made with Portland cement, the two German types of Portland blastfurnace cement, and high-alumina cement. The prisms

made with Portland cement were completely destroyed after eleven years and the high-alumina cement after thirteen years. The Portland blastfurnace cements showed appreciable weakening and loss of material. The strontium-slag cements after fifteen years suffered a very marked softening to a limited depth, with loss of sand and scaling on the edges and surfaces. The barium-cement and barium-slag-cements were unaffected.

The stability of the barium cements in sea-water is explained as follows. The barium oxide formed during the hardening process is converted by magnesium and calcium sulphates in solution to insoluble barium sulphate, magnesia, and lime. Another portion of the barium oxide replaces lime in the slag, producing dibarium silicate and barium calcium silicate. The free lime thus released produces magnesium oxide and calcium sulphate with the salts of sea-water. The barium sulphate and magnesium oxide form a protective layer over the grains of slag.

The strontium, barium, and strontium-barium-high-alumina cements owe their properties mainly to the presence of aluminates of barium and strontium. As in the case of ordinary (calcium) high-alumina cement, hydration leads to the formation of colloidal aluminium hydroxide. The strontium-high-alumina cement is insoluble in water and is an hydraulic material. The strontium-barium-high-alumina cement is partly soluble in water and the barium-high-alumina cement is completely soluble in water; neither of these is hydraulic, they merely become air-hardened as the gel dries out. If the iron content of any of the materials is low enough to produce a melting point above 1,580 deg. C., then the material is a refractory cement.

The strontium-high-alumina cement is a true high-alumina cement in which strontium has replaced calcium. For example, a monoaluminate is present and reacts with water to form distrontiumhydroaluminate (2 SrO. Al_2O_3, nH_2O). The strontium-barium-high-alumina cement has no unusual properties of technical value. The barium-high-alumina cement of low iron content is a refractory cement. Barium aluminates in general have higher melting points than the corresponding calcium aluminates. A compound 3 BaO. 16 Al_2O_3 analogous to 3 CaO. 16 Al_2O_3 occurs. Water completely decomposes all known barium aluminates in a few hours.

A white cement, which is refractory up to 1,770 deg. C., can be made by fusing four parts of alumina with seven parts of barium carbonate. Under the microscope the clinker shows a complex heterogeneous structure. With an aggregate such as magnesite this will produce concrete that is refractory at over 2,000 deg. C.

Barium-high-alumina cement with a high iron content is an air-hardening material which is soluble in water and is not refractory. Concrete made with barium cement (corresponding to Portland cement with barium instead of calcium) and barium-containing aggregate gives twice as much protection against X-rays as does concrete made with ordinary Portland cement and barium-containing aggregate.

Cement Production in Portuguese East Africa.

The capacity of the Secil cement factory in Angola is to be increased from 90,000 tons to 300,000 tons a year. The Zaire works at Lobito has also been authorised to increase production from 90,000 tons to 140,000 tons a year. The consumption of cement in Angola in 1956 was 151,510 tons, of which 64,294 tons were imported, mainly from Portugal, Germany, and Belgium.

Proposed Extension of an Indian Works.

The Shree Digvijay Cement Co., Ltd., of Shree Niwas House, Waudby Road, Fort, Bombay 1, has been authorised to expand the capacity of its factory at Bombay by 200,000 tons per annum.

Proposed Cement Works in Peru.

Compañía de Cementos Arequipa S.A. proposes to build a cement works with a capacity of up to 500 tons a day of Portland cement, Roman cement, and white cement. The address of the company is Coronel Baquero 221, Lima, Peru.

The Cement Industry in Iran.

The Government of Iran has decided to pass to private ownership the cement works now operated by the State, and to provide loans in order to encourage the erection of more cement works.

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